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Compact discs as versatile cost-effective substrates for releasable nanopatterned aluminium films†

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We demonstrate that standard polycarbonate compact disk surfaces can provide unique adhesion to Al films that is both strong enough to permit Al film nanopatterning and weak enough to allow easy nanopatterned Al film detachment using Scotch tape. Transferred Al nanohole arrays on Scotch tape exhibit excellent optical and plasmonic performance.

Introduction

Easy transfer of nanopatterned thin metal films from one substrate to another is an issue of great interest for nanotechnologists and scientists in general. The former can employ contact transfer techniques, such as nanotransfer printing¹ and template stripping,² for fabricating plasmonic and electronic devices and systems at a low cost and high throughput on a variety of substrate materials, including unconventional and flexible supports.^{3,4} A variety of research needs, such as atomic force microscopy (AFM) and scanning electron microscopy (SEM) applications, biosensor development, and self-assembled monolayer (SAM) studies, may also benefit from the availability of ready-to-use, uncontaminated nanostructured metal films just seconds before experiments by a simple transfer procedure from one surface to another.

Contact transfer techniques rely on transferring a metal nanopattern from a stamp or template – typically made of Si or polydimethylsiloxane (PDMS) – to a backing layer by intimate physical contact between surfaces (stamp-metal, metal-

backing). Different interface bonding strengths allow the metal nanopattern to be transferred. Patterned films of noble metals (Au, Ag) can easily be peeled due to their poor adhesion. However, metals prone to form oxygen-rich surfaces, such as Al, exhibit higher adherence, and, therefore, metal film detachment requires the addition of intermediate specific anti-adhesion layers, such as SAMs⁵ and gold films,⁶ which entails additional processing steps and chemistry layer restrictions. This is an important drawback since Al is the ideal material for multiple electronic, optical and plasmonic⁷ uses due to its low cost, good conductivity and broad band optical operation.

Recently, we have reported the fabrication of Al nanohole arrays (NHAs) on conventional polycarbonate (PC) compact disc (CD) surfaces using electron-beam lithography (EBL) and plasma etching.⁸ The NHAs exhibited good optical performance and proved their suitability as plasmonic biosensors for CD-based biosensing platforms. In this paper, we demonstrate for the first time that Al NHAs on a PC CD, fabricated according to the process described in ref. 8, can be directly transferred onto a general purpose adhesive Scotch tape by a simple stick-and-peel procedure under ambient conditions. No specific anti-adhesion layer or treatment is required to allow easy nanopatterned Al film detachment. The morphological and optical qualities of the Al NHAs on Scotch tape are studied. Finally, examples of application of the resulting Al NHA devices on Scotch tape are presented.

Experimental

Nanohole array fabrication on PC CD surfaces

PC square substrates (12 mm × 12 mm) were cut from a 1.2 mm thick standard CD (MPO Iberica, Madrid, Spain) using a dicing saw machine. The PC substrates were washed with detergent in a ultrasonic bath, rinsed in deionized water (DIW) and isopropyl alcohol (IPA) and dried under N₂ flow. Then, an e-beam evaporated 100 nm thick layer of Al was deposited on the flat surfaces (*i.e.*, with no track) of the PC CD substrates.

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† Electronic supplementary information (ESI) available: 1. Optical simulations (Fig. SI.1); 2. Optical coupling via an Al NHA on the Scotch tape (Fig. SI.2); 3. Electrostatics-based opto-mechanical cantilever (Fig. SI.3). Video 1. Transfer of the Al film nanostructured with a nanohole array from a polycarbonate CD surface onto a Scotch tape; Video 2. Opto-mechanical electrostatics-based sensor: electrical attraction. Video 3. Opto-mechanical electrostatics-based sensor: electrical repulsion. See DOI: 10.1039/c4nr06271j

Next, ZEP-520 positive tone EBL resist was spin coated on the Al films at 5000 rpm. The samples were then immediately baked for 10 min at 120 °C. Dot matrix arrays of pitches ranging from 500 to 740 nm were patterned in the resist film by e-beam single-shot exposure using a Crestec CABL-9000C high-resolution EBL system (acceleration voltage = 50 keV, beam current = 1 nA, exposure time = 200 μ s). The exposed resist was developed at 0 °C for 40 s and N₂ dried. Inductively coupled plasma (ICP) chemical dry etching was used to drill holes in the Al layer down to the CD substrate using the patterned ZEP-520 film as a mask. The ICP process was achieved using BCl₃ (20 sccm) and Cl₂ (10 sccm) gases and RF and ICP powers of 100 W. Immediately after the ICP etch, the samples were rinsed in DIW for 5 min to dissolve residual chloride ions. Finally, O₂ plasma treatment was carried out to remove the resist residues and passivate the Al surface.⁸

Transfer printing procedure

The PC CD substrates containing the nanopatterned Al films were fixed on a glass slide by gluing the back side of the PC substrate to the glass with cyanoacrylate-based glue (Loctite, Henkel, USA). A general purpose transparent pressure-sensitive adhesive (PSA) tape (#550 Scotch®, 3M, St. Paul, MN, USA) was used for pattern transfer.

The sticky tape is 50 μ m thick and is composed of a 30 μ m thick bi-oriented polypropylene (BOPP) backing and a synthetic acrylic adhesive (from product data sheet). A 19 mm wide by approximately 4 cm long piece of tape was applied onto the nanopatterned Al surface on the PC CD using finger pressure for approximately 1 min. Then the adhesive tape was peeled off to transfer the metal film from the PC CD surface onto the tape. The pattern transfer process is schematically illustrated in Fig. 1 and recorded in Video 1 (ESI[†]).

Optical transmission spectra measurements

Tapes containing Al NHAs were placed onto one of the four flat inner sidewalls of a square-section quartz cuvette with the tape backing in contact with the cuvette surface. Then, the transmission spectra of the Al NHAs were measured at room temperature (RT) using a Jasco V-650 UV-VIS spectrophotometer with nonpolarized light under normal incidence in the 500–850 nm wavelength range and a spectral resolution of 0.2 nm. The recorded spectra were smoothed using the means movement method (Jasco Spectra Analysis software version 1.53.04) with a convolution width of 15. For bulk refractive index (RI) sensing experiments, the cuvette was filled with different aqueous solutions of citric acid: 0% (DIW, RI = 1.333), 10% w/w (RI = 1.346) and 20% w/w (RI = 1.359).

Surface characterization

Surface morphology was characterized using a FEI Inspect F50 scanning electron microscope (SEM) and a Digital Instruments MultiMode Scanning Probe Microscope Model MMAFM-2 Atomic Force Microscope (AFM) equipped with Veeco probes made of Si, using the tapping mode.

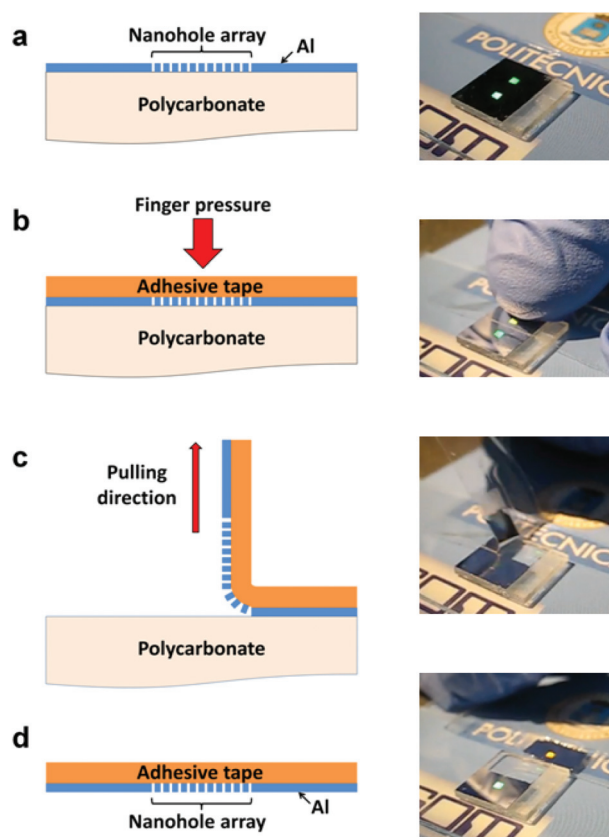


Fig. 1 Schematics (left) of the direct transfer of an Al nanohole array onto a Scotch tape. Photographs on the right show the procedure on a 12 mm \times 12 mm piece of CD with two Al NHAs; Al patterned film transfer is applied to half of the surface containing one Al NHA, which is successfully transferred onto the tape.

Results and discussion

As shown in the photographs of Fig. 1, the nanopatterned Al film is successfully peeled off from the CD substrate along with the adhesive tape. The whole area of the Al film under the tape is completely transferred onto the latter. Fig. 2 shows SEM photographs of a transferred Al NHA surface on Scotch

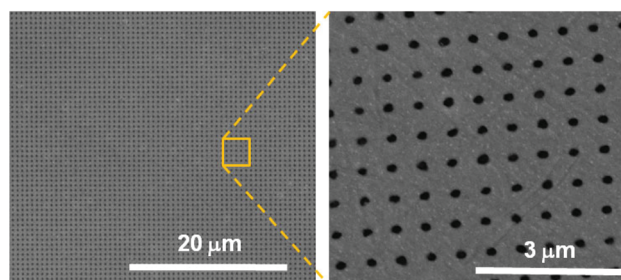


Fig. 2 Scanning electron microscope photograph of the surface of a 625 nm-period Al NHA transferred onto a Scotch tape. The surface exhibits excellent uniformity over large areas.

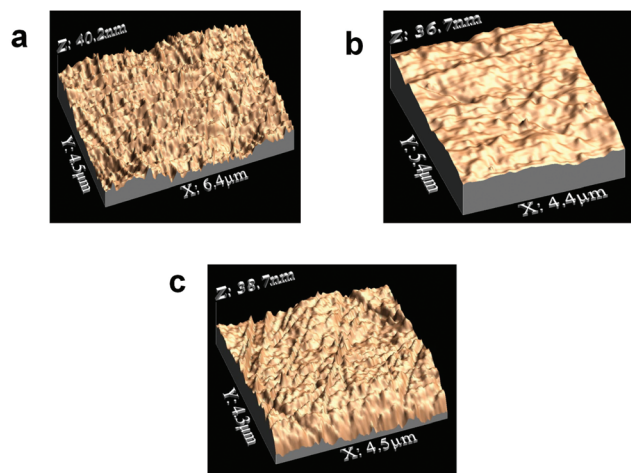


Fig. 3 AFM images of the CD surface (a), Al on CD (b) and Al on tape (c). (a) and (c) exhibit similar roughness, that is, the Al on the tape surface replicates that of the CD from which it has been detached.

tape. Excellent uniformity over a large area is observed, indicating high quality transfer. Surface grooves observed in the magnified SEM picture are attributed to the original CD surface from which the Al film was detached (as shown in AFM images in Fig. 3). AFM surface characterization revealed RMS roughness values for the CD substrate, Al film on the CD and transferred Al film on Scotch tape of 5.5, 2.3 and 5.4 nm, respectively. It should be noted that the CD substrates were used as received, that is, no surface polishing treatment was applied. The detached Al film surface roughness replicates that of the CD surface, indicating good metal wetting of the latter.

Good metal wetting suggests good adhesion between the Al film and CD substrate. In fact, we found that evaporated bare Al films on CD substrates did not, or poorly, detach using the adhesive tape peeling procedure. This result appears to contradict the observed easy detachment of Al films containing NHAs. It is therefore reasonable to attribute the latter to a process step or a combination of process steps carried out during the NHA fabrication. To investigate this, bare Al films were deposited on CD substrates, previously cleaned according to the NHA fabrication process – that is, with IPA and N_2 flow dry –, exposed to different temperatures (RT, 40, 60, 80, 100, 120 and 140 °C) and subjected to tape sticking and peeling off. Temperature exposure targeted at studying the effect of the EBL resist bake (120 °C for 10 min) carried out during NHA fabrication (Experimental section). The results (shown in Fig. 4) indicate that the heating temperature has a role in modifying the Al/CD adhesion strength. No significant Al film detachment occurs for temperatures up to 60 °C; at 80 °C partial peeling is obtained; and full film removal is achieved for 100 °C and 120 °C. At 140 °C the Al film was not removed. The latter result may be related to the glass transition temperature of PC (~145 °C) as the substrate surface softening may increase the metal/PC interface bonding strength.

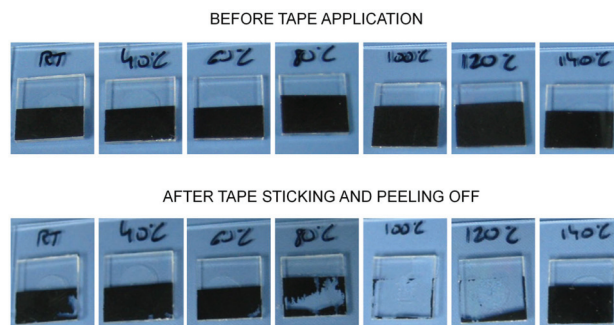


Fig. 4 Photographs of unpatterned Al films on CD substrates before (upper row) and after (bottom row) Scotch tape sticking and peeling off. All substrates were rinsed in IPA and N_2 dried before Al deposition. Then, after Al deposition and before tape sticking, the samples were exposed to different temperatures (from left to right): RT, 40, 60, 80, 100, 120 and 140 °C.

To gain insight into the observed temperature effect, we also deposited bare Al films on CD substrates previously cleaned with IPA, N_2 flow and an additional heating at 80 °C for 10 min (not achieved in the NHA fabrication procedure) to further eliminate IPA from the CD surface. The samples were exposed to 120 °C for 10 min and subjected to the same tape procedure. In this case, no Al film peeling was obtained. This indicates that the presence of IPA molecules on the CD surface before Al deposition also contributes to the weakening of the Al/CD interface adhesion. After the deposition of the Al film, temperatures above 80 °C (the boiling point of IPA is 82 °C) would promote IPA molecule desorption at the metal/CD interface debilitating its bonding strength, in agreement with the results obtained for 80, 100 and 120 °C.

Thus both, IPA rinsing before Al deposition and heating above 80 °C (and below 140 °C) after Al deposition appear to be the necessary and sufficient conditions for Al film detachment. Note that this finding can be the starting point for the development of an adhesive lithography technique for large-scale patterning of Al thin films on CD surfaces. It is clear that further experiments and surface analysis, beyond the scope of this preliminary report, would be required to optimize (sticking pressure, peeling speed and angle, temperature, *etc.*) and fully understand (*e.g.* role of surface roughness and chemistry) the detachment process. It is also important to mention that despite the weakening of the interface adhesion that occurs during the NHA fabrication at the step of EBL resist bake, the Al film-CD adhesion is strong enough to allow subsequent nanofabrication by means of conventional top-down approaches (EBL and plasma etching) as demonstrated in ref. 8.

The transferred Al NHAs on Scotch tape exhibit clear diffraction optical properties in both reflection (Fig. 5a) – revealed as iridescent colours – and transmission (Fig. 5b), corroborating good quality transfer. Calculated and measured transmission spectra of a 500 nm-pitch Al NHA on Scotch tape in air are shown in Fig. 5c. Good agreement between simulation and experimental data is observed. The spectra exhibit three

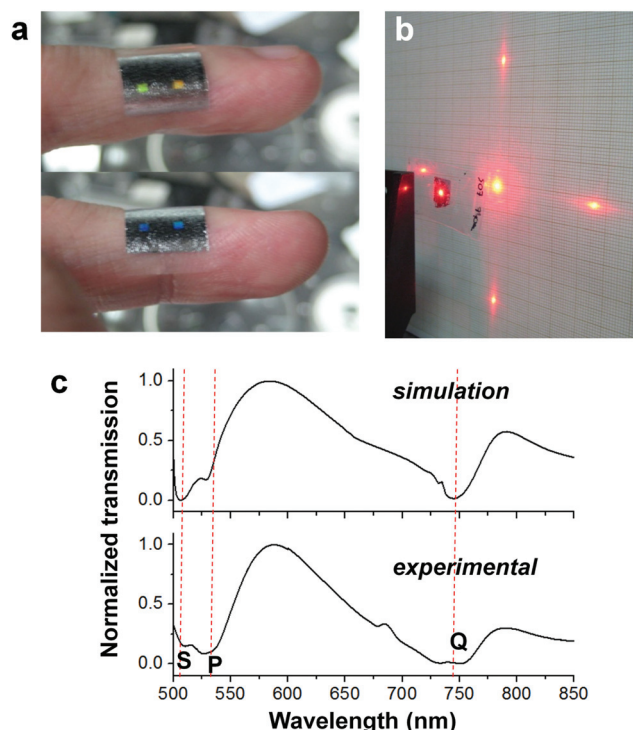


Fig. 5 (a) Photograph of a peeled Scotch tape with an Al film containing two 625 nm-period NHAs adhered conformally onto the little finger. NHA iridescence is clearly observed upon finger rotation. (b) Transmitted diffraction pattern of a 730 nm-period Al NHA on a Scotch tape when illuminated with a 633 nm-wavelength He–Ne laser. (c) Calculated (top) and experimental (bottom) transmission spectra of a 500 nm-period Al NHA on Scotch tape. Resonance features (indicated as S, P and Q) lie close to those predicted by the approximated SPP-grating equation (eqn (1)) (red dashed lines).

main resonance features, referred to as their respective minima: S-wavelength (~ 510 nm), P-wavelength (~ 525 nm) and Q-wavelength (~ 750 nm). Surface plasmon polaritons (SPPs) Bloch waves in a metal grating occur at wavelengths, λ_{SPP} , given by

$$\lambda_{\text{SPP}} \approx \frac{a}{\sqrt{i^2 + j^2}} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (1)$$

where a is the array period, i and j are the grating orders and ϵ_m and ϵ_d are the dielectric functions of the metal and dielectric medium, respectively. Assuming a refractive index of 1.47 for the adhesive material (synthetic acrylic) of the Scotch tape, eqn (1) leads to SPP resonances at 507 nm ($i = \pm 1, j = 0$) for the metal/air interface, 533 nm ($i = \pm 1, j = \pm 1$) and 745 nm ($i = \pm 1, j = 0$) for the metal/acrylic (tape) interface. These values (dashed red vertical lines in Fig. 5c) match approximately the S, P and Q transmission minima wavelengths, indicating effective excitation of SPPs.

The 500 nm-pitch Al NHA on tape was tested as a plasmonic refractometric sensor by immersing it into different aqueous solutions of citric acid. S-wavelength, λ_s , increases with the concentration (Fig. 6), that is, with the solution refractive

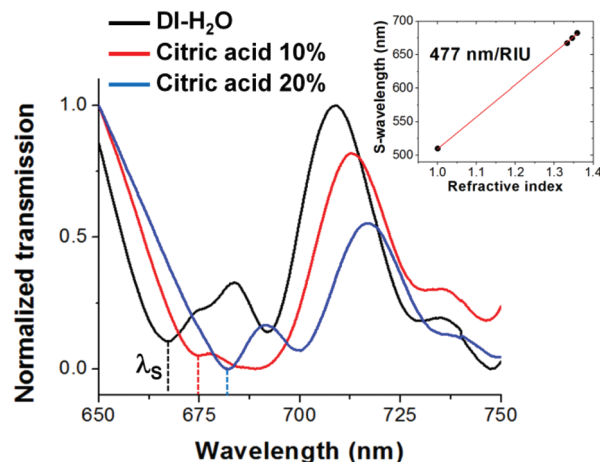


Fig. 6 Measured transmission spectra of a 500 nm-pitch Al NHA on Scotch tape immersed in aqueous solutions of citric acid (0, 10% and 20% w/w). The inset shows a linear fit of λ_s versus the solution refractive index (RI), including air. The bulk RI sensitivity is 477 nm RIU^{−1}.

index. Linear fitting of λ_s versus the solution RI, including the case of air, leads to a bulk sensitivity (linear fit slope) of 477 nm RIU^{−1} (adjusted R -square = 0.9997). This sensitivity value is similar to that measured for a similar 500 nm-period Al NHA fabricated on glass,⁹ which supports the high quality of the transferred Al NHAs and the capability of these devices to be used as plasmonic sensors.

Besides refractometric optical sensing and research applications, releasable ready-to-use Al NHAs can find uses in diverse areas. The stickiness and flexibility of PSA tapes make them particularly suitable for implementing security sticky plasmonic labels, and removable adhesive sensors and optical components capable to be applied onto a variety of material surfaces and shapes. For example, optical coupling to a desired guided-wave object could be readily achieved by sticking a proper Al NHA on its surface (see example in Fig. SI.2†). Thus, no device processing on the object surface, which may be difficult or impossible to carry out, is needed. Another potential application takes advantage of the amenability of adhesive tapes to be electrically charged by peeling them off (triboelectric effect). This feature, besides flexibility and robustness, makes PSA tapes an ideal material platform for implementing electrostatic-opto-mechanical cantilever sensors as shown in Fig. SI.3 and Video 2 and Video 3 (ESI†).

Finally, it should be noted that CDs are highly versatile material platforms as they can provide multiple and simultaneous functionalities in the same support, such as data storage (original and usual use of CDs), microarray optical bio-sensing,¹⁰ and the new function presented here.

Conclusions

We have demonstrated direct transfer of nanopatterned Al films onto an adhesive tape by stripping them from PC CD sur-

faces. The transfer process consists of simply sticking the tape on the Al nanopattern and peeling off. Easy Al film detachment from the CD surface is attributed to a weakening of the Al/CD interface bonding due to the combined effects of two particular process steps carried out during the NHA fabrication on CD substrates: (i) IPA substrate rinsing before Al deposition and (ii) baking at 120 °C after Al deposition. Transferred Al NHAs on tape show excellent surface uniformity over large areas and exhibit good optical and plasmonic performance. To our knowledge, this is the first demonstration of the suitability of commercially available standard CDs as substrates for high quality, easily releasable Al films patterned on the nanoscale. Low cost, versatility and large-area process capability of both, CD and Al materials, and the simplicity of the release procedure make these results an important step to push forward the introduction and affordability of nanotechnology-based consumer products in the market for a wide range of applications.

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